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(54) Title: NOVEL TRANSITION METAL COMPLEXES AND METHOD FOR PREPARING THEM			
(57) Abstract			
<p>A transition metal complex having a general formula of $M(RNpy)_xX_z$ where M is a transition metal selected from groups IVb-VIb of The Periodic Chart of the Elements, RNpy is unsubstituted or substituted amidopyridine derivative, X is a ligand having a valency of 1, y is 1-4, z is 0-5 and y+z is 3-6. This complex can be used for polymerization of olefins together with acceptor compound, such as methylalumoxane.</p>			

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Novel transition metal complexes and method for preparing them

5 The present invention deals with new complexes of transition metals and a method for preparing them. The invention concerns also a catalyst system of transition metal complexes for polymerizing ethylenically unsaturated monomers. Further the invention concerns a method for homo or copolymerizing ethylenically unsaturated monomers in the presence of a catalyst system comprising a transition metal complex and an organometallic
10 compound.

Olefin polymerization with Ziegler-Natta catalysts has been used for a long time. These catalysts are based on complex systems of organoaluminium compounds and at least one transition metal compound, especially titanium. Ziegler-Natta catalysts are very sensitive to
15 catalyst poisons, especially for oxygen and water. The structure of the real catalyst is at least partly still unknown. Based on the wide molecular weight distribution of the produced polymers, it has been proposed that the traditional Z-N catalysts contain several, structurally different active sites (see G. Fink, R. Mülhaupt and H.H. Brintzinger, editors in Ziegler-Catalysts, Springer-Verlag, Berlin Heidelberg, 1995).

20

Recently catalysts based on metallocene compounds and alumoxane compounds have been developed. In these catalysts a transition metal atom, normally zirconium, hafnium or titanium is sandwiched between parallel planar cyclopentadienyl groups. The activity of metallocenes is greatly improved by stabilizing with a bulky non-coordinating MAO anion.
25 Operating in the presence of these catalysts polymers having a narrow molecular weight distribution with improved yield can be obtained. Metallocene catalysts are extremely active. They are structurally well characterized and typical for them is that they contain a single active center which results in very homogenous polymer. This can be seen as narrow molecular weight distribution. (see M. Bochmann, J. Chem. Soc. Dalton. Trans.,
30 1996,225).

European patent application 0687693 discloses amidinato complexes, which have allylically connected resonance structures and perform high molecular weight distribution with moderate activity in olefin polymerization.

- 5 The purpose of the present invention is to find new alternative complex systems, which are more active in the polymerization or copolymerization of olefins and other monomers than conventional Ziegler-Natta catalysts. The new complexes also have advantages of metallocenes, especially single active site. The purpose of the invention is also a transition metal complex which can be prepared by a method which is very easy and economical.
- 10 Still another purpose of the invention is a catalyst system comprising a novel transition metal complex and an activator compound for polymerization of ethylenically unsaturated monomers, especially α -olefins.

According to the present invention it has been found that amidopyridine ligands offer an electronically and sterically rigid structure with heterocyclic π -donor and amido bond without coordination of conjugated double bonds seen in the known metallocene complexes and amidinato complexes according to EP687693. The complexes according to the invention differ significantly from the previously patented ones both structurally and in catalytic performance producing polymers with a very narrow molecular weight distribution and good activity.

The transition metal complex according to the invention is characterized in that it has a general formula (I)



where

M is a transition metal selected from groups IVb-VIb of The Periodic Chart of the Elements,

30

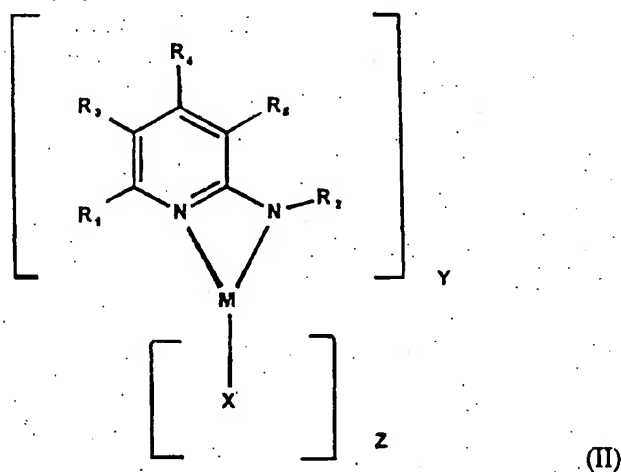
RNpy is unsubstituted or substituted amidopyridine derivative,

X is a ligand having a valency of 1, and

y is 1-4, z is 0-5 and y+z is 3-6.

5 Transition metal M can be selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo or W.

The complexes of the present invention can be presented also by a general formula of (II):



where

15 R_2 is selected from hydrogen or linear, branched or cyclic C_1 - C_{25} alkyl group or cyclic C_1 - C_7 alkylene group connected to groups R_1 , R_3 , R_4 , or R_5 as defined below, or silyl alkyl $SiRR'R''$ or boron alkyl BRR' where R, R' and R'' are as defined for R_1 , R_3 , R_4 and R_5 .

20 R_1 , R_3 , R_4 and R_5 are same or different groups selected from hydrogen, linear, branched or cyclic C_1 - C_{25} alkyl group, or a cyclic C_1 - C_7 alkylene group connected to R_1 , R_2 , R_3 , R_4 , or R_5 , or substituted main group element (B, C, Si, N, O, P, As, Sb, Pb..) with a substituent as R_1 - R_5 .

M is a transition metal selected from Ti, Zr, Hf, V, Nb, Ta, Mo, Cr or W.

X groups are independently halide and/or oxo group or alkyl as R_2 , or $-NRR'$ where R and R' are as R_2 , and X can also act as a bridge between two or more $M(RNpy)_yX_{z-1}$ units, and

5

y is 1-4 and z is 0-5 and $y+z$ is 3-6.

Preferably X is halide, such as chloride, bromide, iodine or fluoride, or methyl or ethyl group. In the case of V, Mo, W it can be an oxo group.

10

Typical examples of compounds according to formula (I) are the following compounds, where Py = pyridine (pyridyl), Bz = benzyl and Ph = phenyl:

2-(phenylamino)pyridiniumtetrachloro-2-(phenylamido)pyridine titanate(IV)
15 $[PhNHPyH][TiCl_4(PhNPy)]$,

di- μ -chlorodichlorotetrakis[2-(phenylamido)pyridine]dizirconium(IV)
 $[Zr_2Cl_4(PhNPy)_4]$,

20 tetrakis[2-(phenylamido)pyridine]hafnium(IV)
 $[Hf(PhNPy)_4]$,

trichlorobis[2-(phenylamidopyridine)]niobium(V)
 $[NbCl_3(PhNPy)_2]$,

25

bis[2-(benzylamido)pyridine]trichloroniobium(V)
 $[NbCl_3(PyNBz)_2]$,

trichlorobis[2-(phenylamido)pyridine]tantalum(V)
30 $[TaCl_3(PhNPy)_2]$,

trichlorobis(2-phenylamido-6-phenylaminopyridine-N,N')tantalum(V)

[TaCl₃(PhNPyNHPh)₂],

bis[2-(benzylamido)-4-methylpyridine]trichlorotantalum(V)

[TaCl₃(PyNBz)₂],

5

bis[2-(benzylamido)-4-methylpyridine]trichlorotantalum(V)

[TaCl₃(4-MePyNBz)₂], and

trichloro-2-(phenylamido)pyridineoxotungsten(VI)

10 [WCl₃O(PhNPy)].

The invention concerns also a method for preparing the complexes above, which is characterized in that 2-(phenylamido)pyridine or 2-(benzylamido)pyridine is reacted with a halide or halide derivative of a transition metal selected from groups IVb-VIb. Preferably the transition metal is selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, or W. The halide is selected from chloride, bromide, iodine or fluoride, preferably chloride.

According to a preferable embodiment of the invention the catalyst complexes are prepared by using 2-(phenylamido)pyridine, 2-(benzylamido)pyridine or their derivatives, and halides of transition metals as starting materials. In the preparation method solvents can be used or not used. In the first mentioned case 2-(phenylamido)pyridine is dissolved in a proper solvent. The solution can be cooled down to -70 °C - 0 °C before contacting with halide. Alternatively the solution can be carried out at room temperature or at higher temperature.

25

The reaction between the amidopyridine and transition metal halide can be carried out at a temperature between 50-150 °C or refluxing at the boiling temperature of the solvent. The reaction time can vary from 10 min to 10 hours, preferably 1-3 h.

30 As solvents typical aromatic solvents like toluene, benzene or xylene can be used.

The starting materials can be contacted also without solvents by melting them together. The temperature can in this case vary between 50 °C and 200 °C, preferably however 0-10 °C above the melting point of the aminopyridine ligand used. The reaction time is not critical and it can vary between 10 min to 10 hours, preferably between 1 to 3 hours.

5

During the reaction HCl (gas) or ligand-HCl adducts are developed. These can be removed by extracting with a proper solvent, such as toluene. The catalyst complexes of the invention can be obtained in conventional way, for example by crystallization methods.

10 The invention concerns also a catalyst system for homo or copolymerizing ethylenically unsaturated monomers. The catalyst system according to the invention is characterized in that it comprises

A) a transition metal complex having a general formula (I)

15



where

20 M is a transition metal selected from groups IVb-VIb of The Periodic Chart of the Elements,

RNpy is unsubstituted or substituted amidopyridine derivative,

X is a ligand having a valency of 1, and

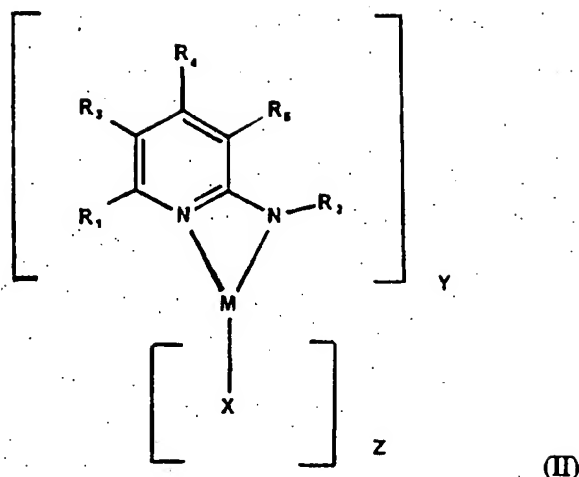
25

y is 1-4, z is 0-5 and y+z is 3-6, and

(B) an acceptor compound for component X as an activator.

30 Transition metal M can be selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo or W.

The component (A) can be presented also by a general formula (II)



where

5

R_2 is selected from hydrogen or linear, branched or cyclic C_1 - C_{25} alkyl group or cyclic C_1 - C_7 alkylene group connected to groups R_1 , R_3 , R_4 or R_5 as defined below, or silyl alkyl $SiRR'R''$ or boron alkyl BRR' where R , R' and R'' are as defined for R_1 , R_3 , R_4 and R_5 .

10 R_1 , R_3 , R_4 and R_5 are same or different groups selected from hydrogen, linear, branched or cyclic C_1 - C_{25} alkyl group, or a cyclic C_1 - C_7 alkylene group connected to R_1 , R_2 , R_3 , R_4 or R_5 , or substituted main group element (B, C, Si, N, O, P, As, Sb, Pb..) with a substituent as R_1 - R_5 .

15 M is a transition metal selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, or W,

X groups are independently halide and/or oxo group or alkyl as R_2 , or $-NRR'$ where R and R' are as R_2 , and X can also act as a bridge between two or more $M(RNpy)_yX_{z-1}$ units, and-

20 y is 1-4 and z is 0-5 and $y+z$ is 3-6.

Preferably X is halide, such as chloride, bromide, iodine or fluoride, or methyl or ethyl group. In the the case of V, Mo, W it can be an oxo group.

The component (B) in the catalyst system for homo or copolymerizing ethylenically unsaturated monomers can be any usable acceptor compound for ligand X in the formulas above. These acceptor compounds are commonly lithium, boron or aluminium organometallic compounds such as alkyl or alkyl halide derivatives or salt containing ammonium or carbo cationic part combined with weakly or non-coordinating anions(s). The anions are commonly carbaboranes, fluoro anions of boron or phosphor or tetraalkyl boron complexes. Preferably (B) is an organometal compound, for example organoaluminium compound. Preferable activators are, for example, alumoxane compounds having the formula of $R-(Al(R)-O)_n-Al(R)_2$, where n is 1-40, m is 3-40 and R is C_1-C_8 alkyl group. Preferably R is methyl and preferable activator is methylalumoxane (MAO). Illustrative, but not limiting examples for component (B) are methylalumoxane, $AlClEt_2$, $PbEt_4$, butyllithium and salts containing $[CPh_3]^+$ or $[NHMe_2PH]^+$ cation and $[PF_6]^-$, $[BF_4]^-$, nido-carbaborane $C_2B_9H_{13}$, $[B(C_5F_5)]^-$ or $[BPh_4]^-$ anion.

15

The activator can be applied according to the methods known in the art before polymerization or during the polymerization.

The catalysts according to the invention can be used as homogenous systems or they can be deposited on inorganic or organic carrier. Silica, alumina or polymeric carriers like polyethylene or polystyrene can be used as supports.

The catalysts according to the invention are suitable for homo and copolymerization of all olefinic monomers, for example ethylene, propylene, butene, pentene, hexene, 1-methyl-1-pentene or alike. Further they can be used for polymerization of cycloolefins like norbornene and dienes like butadiene, 1,4-hexadiene or 1,5-hexadiene.

The polymerization can be carried out by slurry, gas phase or solution processes either batchwise or continuously. The polymerization conditions are not critical. Thus polymerization temperatures from 0 to 150 C, preferably 50-110 C, and pressures up to 1000 bar, preferably 5-70 bar can be used.

Typical for the polymers according to invention is very narrow molecular weight distribution, which can be seen from the Table, and a good activity better than that of most Ziegler-Natta catalysts and many metallocene based systems.

5 Examples

Syntheses of the compounds, which have been characterized with single crystal X-ray analyses.

10 Example 1

2-(Phenylamino)pyridiniumtetrachloro2-(phenylamido)pyridine titanate(IV)
[PhNHPyH][TiCl₄(PhNPy)]

15 2-(Phenylamino)pyridine was dissolved to toluene (40 ml). Solution was cooled down to -20 °C. Two molar equivalents of titanium(IV) chloride was added. Temperature of the solution was raised to 40 °C in 45 minutes and kept for one hour. The reaction mixture was filtered. Dark red prismatic crystals suitable for single crystal measurements were obtained at room temperature in 15 hours.

20

Example 2

Di-μ-chlorodichlorotetrakis[2-(phenylamido)pyridine]-dizirconium(IV)
[Zr₂Cl₄(PhNPy)₄]

25

Ligand precursor, 2-(phenylamino)pyridine (9.32 g, 54.8 mmol), was suspended to 100 ml of toluene and cooled down to -50°C. Zirconium(IV)chloride (6.20 g, 26.8 mmol) was added to the suspension. Temperature of the continuously stirred suspension was allowed to rise into room temperature in 60 minutes. Mixture which started to turn orange colored
30 was then refluxed for 45 minutes. The orange solution was separated from oily, amorphous like precipitation and filtered. Large orange crystals were obtained in 2 hours. Yield of the

crystalline homomorphous material was ca. 10%. Mass spectra: (EI) m/z 500 ($ZrCl_2(PhNPy)_2^+$), 463 ($ZrCl(PhNPy)_2^+$).

Example 3

5

Tetrakis[2-(phenylamido)pyridine]hafnium(IV)
[Hf(PhNPy)₄]

2-(Phenylamino)pyridine (1.92 g, 11.3 mmol) was suspended to 70 ml of toluene and 10 cooled down to -50°C. Hafnium(IV) chloride (0.92 g, 2.9 mmol) was added to the vigorously stirred suspension. Solution slowly turned to pale yellow colour when its temperature was allowed rise to room temperature. Solution was heated 2 hours at 90°C. Solution was filtered and pale yellow prismatic crystals were obtained after 20 hours.

15 Example 4

Trichlorobis[2-(phenylamidopyridine)]niobium(V)
[NbCl₃(PhNPy)₂]

20 2-Phenylaminopyridine (7.30 g, 42.9 mmol) was suspended to 70 ml of toluene. Niobium(V)chloride (3.72 g, 13.8 mmol) was added to the suspension. Solution which rapidly turned to intense purple was heated 60 minutes at 90 °C, 50 ml of toluene was added and solution was stirred 2 hours at room temperature. Again part of the product was amorphous and insoluble in toluene. Solution was filtered and purple prismatic crystals 25 were obtained in 10 hours. Yield 2.3 g (31%). Mass spectra: (EI) m/z 536 ($NbCl_3L_2^+$), 367 ($NbCl_3L^+$)

Example 5

30 Bis[2-(benzylamido)pyridine]trichloroniobium(V)
[NbCl₃(PyNBz)₂]

Niobium(V)chloride, 2.36 g (8.73 mmol) and 2-(benzylamino)pyridine 3.22 g (17.3 mmol) were melt at 100 °C for 30 minutes and extracted to toluene (60 ml) with refluxing for 2 hours. Toluene solution was separated from oily purple-black amorphous residue and filtered. Purple crystals where obtained in 15 hours. Estimated yield was 10-15 %.

5

Example 6

Trichlorobis[2-(phenylamido)pyridine]tantalum(V)
[TaCl₃(PhNPy)₂]

10

2-Phenylaminopyridine (2.88 g, 16.9 mmol) was suspended to 70 ml of toluene and cooled down to -50 °C. Tantalum(V)chloride (3.03 g, 8.46 mmol) was added to the suspension. Temperature of the suspension was raised in 2 hours up to 90°C. At -10°C solution began to change the colour red. After heating 90 minutes the solution was filtered. Dark red
15 crystal started to grow in 12 hours. Yield was 2.9 g (54 %). Mass spectra: (EI) m/z 624 (TaCl₃L₂⁺), 589 (TaCl₂L₂⁺), 457 (TaCl₃L⁺)

Example 7

20 Trichlorobis(2-phenylamido-6-phenylaminopyridine-N,N')tantalum(V)
[TaCl₃(PhNPyNHPh)₂]

2,6-bis(phenylamino)pyridine (2.14 g, 8.19 mmol), which was prepared as described previously (M. Hamana, M. Yamazaki, Yakugaki Zasshi, 81, 1961, 574), was dissolved to
25 toluene (40 ml). Solution was cooled down to -20 °C. Tantalum(V) chloride (1.46 g, 4.08 mmol) was added. Temperature of the solution was raised to 40 °C in 45 minutes and kept for one hour. The reaction mixture was filtered. Dark red prismatic crystals suitable for single crystal measurements were obtained at room temperature in 15 hours.

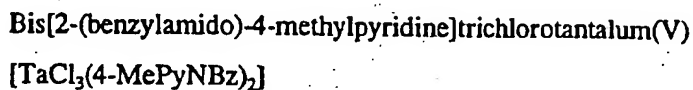
30 Example 8

Bis[2-(benzylamidopyridine)]trichlorotantalum(V)



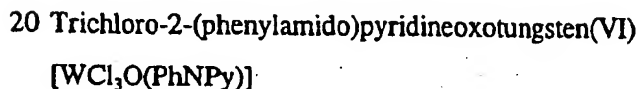
Tantalum(V)chloride, 1.36 g (3.89 mmol) and 2-(benzylamino)pyridine (Mp 95-97 °C), 1.47 g (7.97 mmol) were heated at 100 °C. Melt started to red immediately. After one hour 30 ml of toluene was added, the solution was refluxed for 2 hours, and filtered when hot through Celite. Solution was kept at room temperature and a few drops of n-hexane was added to the solution. Intense red crystalline blocks were obtained in 20 hours. Estimated yield was 50-55 %.

10 Example 9



15 The title compound was prepared analogously to Example 8, but at the temperature of 80 °C.

Example 10



2-(Phenylamino)pyridine (4.10 g, 24.1 mmol) and tungsten(V)-oxotetrachloride (3.20 g, 9.38 mmol) were heated in toluene (50 ml) suspension for 25 minutes at 80 °C. Solution was then filtered and evaporated to reduced volume (30 ml). Large black crystalline blocks with average size over 1 mm in each dimension were obtained at room temperature in 10 hours.

Example 11

30

The compound prepared in Example 8 (Catalyst A) and compound prepared in Example 4 (Catalyst B) as toluene solvates were tested for ethylene polymerization. The catalysts were

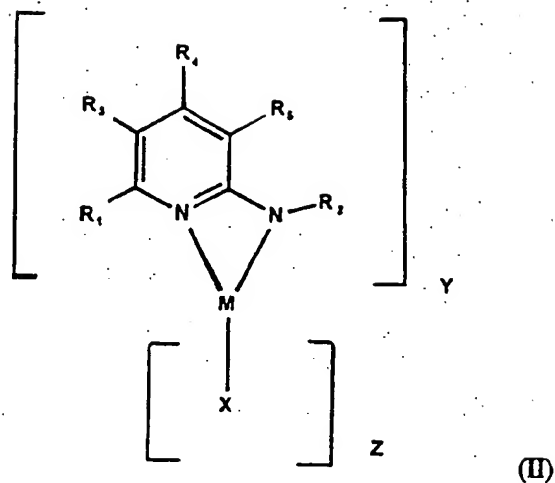
weighed to the polymerization reactor, where also methylaluminiumoxane (MAO) was added as cocatalyst so that Al/Ta (Al as MAO) ratio was 2000 mol/mol. The polymerization was carried out in 300 ml toluene. Ethylene pressure was 5.0 bar. The polymerization conditions and results are presented in the following table.

5

10

Table

Cat.	Amount mg	T °C	Time min	Yield g	Activity kgPE/ molTa/h	M _w g/mol	M _w /M _n	T _m °C
A	10.0	30	20	3.7	800	201200	2.5	137.7
A	5.0	60	7	3.9	5000	93800	2.0	135.4
A	2.0	60	30	2.5	1900	84900	1.9	135.3
A	1.0	60	30	1.0	1500	82800	1.9	134.8
B	5.0	60	7	5.0	7700	90700	1.9	134.8
B	2.0	60	7	2.5	9600	86500	1.9	134.7
B	1.0	60	30	3.2	5800	84500	1.9	135.3
B	1.0	80	7	3.1	23900	66100	1.8	133.9
B	1.0	30	30	0.5	900	115400	1.9	136.3



where

R_2 is selected from hydrogen or linear, branched or cyclic C_1 - C_{25} alkyl group or cyclic C_1 - C_7 alkylene group connected to groups R_1 , R_3 , R_4 or R_5 as defined below, or silyl alkyl $SiRR'R''$ or boron alkyl BRR' where R , R' and R'' are as defined for R_1 , R_3 , R_4 and R_5 .

R_1 , R_3 , R_4 and R_5 are same or different groups selected from hydrogen, linear, branched or cyclic C_1 - C_{25} alkyl group, or a cyclic C_1 - C_7 alkylene group connected to R_1 , R_2 , R_3 , R_4 or R_5 , or substituted main group element (B, C, Si, N, O, P, As, Sb, Pb...) with a substituent as R_1 - R_5 .

M is as defined above,

X groups are independently halide and/or oxo group or alkyl as R_2 , or $-NRR'$ where R and R' are as R_2 defined above, and X can also act as a bridge between two or more $M(RNpy)_yX_{z-1}$ units.

y is 1-4, z is 0-5 and $y+z$ is 3-6.

20

5. A complex according to claims 1-4, characterized in that X is halide or alkyl as R_2 , or $-NRR'$ where R and R' are as R_2 .

6. A method for preparing transition metal complexes according to claims 1-5, characterized in that 2-(phenylamido)pyridine or 2-(benzylamido)pyridine is reacted with a halide or halide derivative of a transition metal selected from groups IV-VIb.
7. A method according to claim 6, characterised in that the transition metal is selected from is Ti, Zr, Hf, V, Nb, Ta, Cr, Mo or W.
8. A method according to claims 6-7, characterized in that the halide is selected from chloride, bromide, iodine, fluorine or oxy derivative thereof.
9. A method according to claims 6-8, characterized in that the reaction is carried out at a temperature of 50-150 °C.
10. A method according to claims 6-8, characterized in that the reaction is carried out without solvent in a melt of starting materials.
11. A method according to claim 10, characterized in that the reaction is carried out at a temperature between 50-200 °C.
12. A catalyst system for homo or copolymerizing ethylenically unsaturated monomers, characterized in that it comprises
- A) a transition metal complex having a general formula (I):
- $$M(RNpy)_yX_z \quad (I)$$
- where
- M is a transition metal selected from groups IVb-VIb of The Periodic Chart of the Elements,
- RNpy is unsubstituted or substituted amidopyridine derivative,

X is a ligand having a valency of 1, and

y is 1-4, z is 0-5 and y+z is 3-6, and

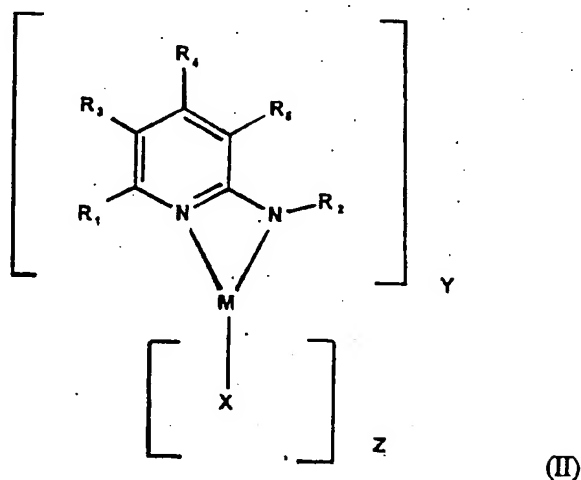
5 (B) an acceptor compound for component X as an activator.

13. A catalyst system according to claim 12, characterized in that the transition metal M is selected from Ti, Zr, Hf, V, Nb, Ta, Cr or W.

10 14. A catalyst system according to claims 12 or 13, characterized in that X is selected from chloride, bromide, iodine, fluoride or oxy derivative thereof.

15. A catalyst system according to claims 12-14, characterized in that component (A) has a general formula (II):

15



where

R₂ is selected from hydrogen or linear, branched or cyclic C₁-C₂₅ alkyl group or cyclic C₁-C₇ group connected to groups R₁, R₃, R₄ or R₅ as defined below, or silyl alkyl SiRR'R'' or boron alkyl BRR' where R, R' and R'' are as defined for R₁, R₃, R₄ and R₅.

R₁, R₃, R₄ and R₅ are same or different groups selected from hydrogen, linear, branched or cyclic C₁-C₂₅ alkyl group, or a cyclic C₁-C₇ alkylene group connected to R₁, R₂, R₃, R₄

or R_5 , or substituted main group element (B, C, Si, N, O, P, As, Sb, Pb..) with a substituent as R_1-R_5 ,

M is a transition metal as defined above,

5

X groups are independently halide and/or oxo group or alkyl as R_2 , or $-NRR'$ where R and R' are as R_2 defined above, and X can also act as a bridge between two or more $M(RNpy)_zX_{z-1}$ units.

10 y is 1-4, z is 0-5 and $y+z$ is 3-6.

16. A catalyst system according to claim 15, characterized in that X is selected from chloride, bromide, iodine, fluoride or oxy derivative thereof.

15 17. A catalyst system according to claims 12-16, characterized in that component (B) is an organometal compound, preferably organoaluminium compound.

18. A catalyst system according to claim 17, characterized in that component (B) is an alumoxane compound having the formula of $R-(Al(R)-O)_n-Al(R)_2$ where n is 1-40, m is 3-
20 40 and R is C_1-C_8 alkyl group.

19. A catalyst system according to claim 18, characterized in that R is a methyl group.

20. A method for homo or copolymerization of ethylenically unsaturated monomer in the
25 presence of a catalyst system according to claims 12-19.

21. A method according to claim 20, characterized in the catalyst system is used as a homogenous system or supported on inorganic or organic carrier.

30 22. A method according to claim 20-21, characterized in that the monomer is one or more monomer selected from ethylene, propylene, butene, pentene, hexene, 4-methyl-1-pentene, cycloolefins like norbornene and dienes like butadiene, 1,4-hexadiene or 1,5-hexadiene.